Egyptian Journal of Aquatic Research (2016) 42, 121–131

HOSTED BY

ELSEVIER

National Institute of Oceanography and Fisheries

Egyptian Journal of Aquatic Research

http://ees.elsevier.com/ejar
www.sciencedirect.com

FULL LENGTH ARTICLE

Distribution and sources of *n*-alkanes and polycyclic aromatic hydrocarbons in shellfish of the Egyptian Red Sea coast

Ahmed El Nemr *, **Abeer A. Moneer, Safaa Ragab, Amany El Sikaily**

Marine Pollution Department, Environmental Division, National Institute of Oceanography and Fisheries, Kayet Bey, Elanfoushy, Alexandria, Egypt

Received 6 April 2016; revised 19 May 2016; accepted 23 May 2016
Available online 21 June 2016

KEYWORDS

Aromatic hydrocarbons;
n-Alkanes;
Shellfish;
Red Sea;
Suez Gulf;
Aqaba Gulf

Abstract Aromatic hydrocarbons and *n*-alkanes were analyzed in shellfish collected from 13 different sites along the Egyptian Red Sea coast. All samples were analyzed for *n*-alkanes (C_8–C_{40}) and polycyclic aromatic hydrocarbons (EPA list of PAHs). *n*-Alkanes in shellfish samples from 13 locations were found to be in the range of 71.0–701.1 ng/g with a mean value of 242.2 ± 192.1 ng/g dry wt. Different indices were calculated for the *n*-alkanes to assess their sources. These were carbon preference index (CPI), average chain length (ACL), terrigenous/aquatic ratio (TAR), natural *n*-alkane ratio (NAR) and proxy ratio (P_{aq}). Most of the *collected samples of n*-alkanes were discovered to be from natural sources. Aromatic hydrocarbons (16 PAHs) from 13 sites varied between 1.3 and 160.9 ng/g with an average of 47.9 ± 45.5 ng/g dry wt. Benzo(a)pyrine (BaP), a cancer risk assessment, was calculated for the PAHs and resulted in ranges between 0.08 and 4.47 with an average of 1.25 ng/g dry wt.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and *n*-alkanes are marine environment chronic constituents and their concentrations have considerably increased due to anthropogenic activities. This caused undesirable effects, especially in coastal areas adjacent to highly populated urban zones. *n*-Alkanes consist of saturated and straight carbon chains of C_6–C_{40} which contain even and odd carbon numbers that indicate anthropogenic and natural sources of hydrocarbon. The United Nation Environmental Program (UNEP) gave guidelines to identify the levels of harmless (< 10 μg/g) and harmful (> 10 μg/g) *n*-alkanes in marine sediment.

PAHs are organic compounds that result from the partial combustion of organic matter (pyrolytic), and oil and its derivative (petrogenic) sources. Pyrogenic PAHs are characterized by the occurrence of PAHs that carry a heavy set of molecular weights, while petroleum hydrocarbons are dominated by PAHs of the lowest molecular weight (Neff, 1979). They are widely dispersed in the marine environment, particularly in harbors, dockyards, marinas, estuaries and other shallow coastal areas with anthropogenic inputs (El Nemr, 2005,

* Corresponding author.
E-mail addresses: ahmedmoustafaelnemr@yahoo.com, ahmed.m.elnemr@gmail.com (A. El Nemr).

Peer review under responsibility of National Institute of Oceanography and Fisheries.

http://dx.doi.org/10.1016/j.ejar.2016.05.003

2008, 2011). PAHs have been subjected to remediation studies and risk assessment, due to their mutagenic and carcinogenic effects. Therefore, PAHs tend to swiftly be absorbed into the particles and fat tissues of filtrating organisms like mussels and oysters (Zemanek et al., 1997). PAHs are easily absorbed by living beings Due to their high octanol/water partition coefficient (K_{ow}). PAHs can be metabolized into compounds that are detectable in fluids and can be used as biomarkers of the exposure to the PAHs (Nudi et al., 2010). The evaluation and comparison levels of PAHs and their temporal changes in a marine coastal region are very important from an environmental point of view (El Sikaily et al., 2003; Salem et al., 2014). Mussels have been widely used for the monitoring of toxic pollutant levels in coastal environment (Saad et al., 2015).

The aim of the present work is to investigate the precedence of *n*-alkanes and PAHs in the collected shellfish from the Red Sea coast (Egypt) and also, to determine the most polluted regions, diagnose the sources of these pollutants and calculate the cancer risk assessment of these compounds to draw a complete picture of the pollution in these regions and then try to find the best way for treatment.

Materials and methods

The sampling cruise took place in August 2011, that covered about 1700 km (Fig. 1). 13 sampling locations were selected to coverage the studied area. The collected shellfish species and their lipid and water contents are listed (Table 1). There was a wide variation of collected species due to the diversity of the environmental conditions and the biodiversity of the sampling locations. Flesh of the shellfish samples of similar species in each site was scraped out of the shell and dissected. All the soft tissues of the 30–40 individual shellfish were mixed well into a composed sample and then dried in an open oven at 50 °C. The dried sample (5 g) was extracted in methanol (200 ml) for 8 h with Soxhlet extractor. 0.8 M KOH (15 ml) and distilled water (25 ml) were added to the extraction. Then the reflux continued for two more hours to saponify the lipids. The mixture obtained was extracted three times with *n*-hexane (50 ml, each) in a separatory funnel. The *n*-hexane was then combined and sodium sulfate anhydrous was added, filtered and finally concentrated under vacuum down to about 10 ml at 40 °C, followed by a concentration using nitrogen gas streaming 1 ml volume. A column chromatography was prepared using silica gel (10 g), followed by aluminum oxide (10 g) and finally 1 g of sodium sulfate anhydrous (Kelly et al., 2000; El Nemr et al., 2004, 2012).

The concentrated extract (1 ml) was sequentially eluted with 25 ml of *n*-hexane belonging to the fraction of *n*-alkaines (F1), then 50 ml of dichloromethane-*n*-hexane (1:9) belonging to the PAHs fraction (F2). The two fractions (F1 and F2) were concentrated to 1 ml each for the GC–MS analysis.

The blanks of 500 ml of solvent that were used were concentrated to 1 ml and then analyzed by gas chromatography as previous reported by El Nemr et al., 2014. Gas chromatography Shimadzu Class LC-10 equipped with Shimadzu Autoinjector, split/splitless injector and a fused silica capillary B-5 (30 m, 0.32 mm, 0.17 μm) 100% dimethylpolysiloxane. The temperature was programed from 60 to 300 °C with a rate of 5 °C min^{-1} and was then maintained at 300 °C for 25 min.

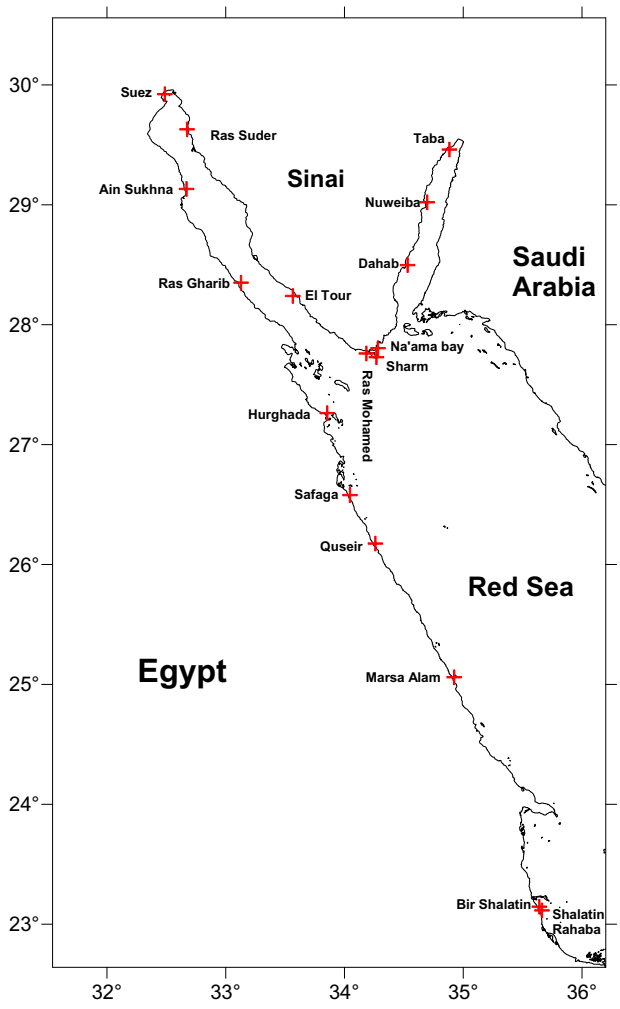

Figure 1 Map of the samples location along the Suez Gulf, the Aqaba Gulf and the Red Sea proper.

The injector and detector temperatures were set at 280 and 300 °C, respectively. Helium was used as the carrier (1.5 ml min^{-1}) and nitrogen as the make-up (60 ml min^{-1}) gas. 2 μL volume of each sample was injected in the split mode (10:1) and the purge time was one minute. Identification and quantification of 16 PAH compounds were based on matching their retention time with a mixture of PAH standards. Compound identification was confirmed by GC coupled to mass spectrometry (Trace DSQ II Ms. with capillary column: Thermo TR-35 MS Mass Selective Detector).

To validate the analytical method used in this study and the accuracy of the results, 6 analyses were made on the PAH compounds in the reference materials, IAEA – 406 (organochlorine compounds, petroleum hydrocarbons in tuna homogenate sample). The recovery efficiencies ranged from 95.22% to 98.93% for IAEA – 406 (Table 2).

Results and discussions

Distribution and sources of ***n****-alkanes*

The sampling locations for the shellfish and their types are listed in Table 1 and the concentrations of *n*-alkanes are

Table 1 Species, total lipid and water contents in the shellfish samples collected from the Gulf of Suez, Gulf of Aqaba and The Red Sea Proper coasts.

Location	Species	Lipid contents %	Water contents %
Taba	*Patella nigrolineata*	9.53	80.48
Dahab	*Morulasquamosa*	1.08	76.16
Na'ama Bay	*Lepidochitoncinereus*	8.48	80.06
Ras Mohamed	*Lepidochitoncinereus*	13.1	76.8
El Tour	*Neritawaigiensis*	4.86	76.08
Ras Suder	*Neritawaigiensis*	4.95	77.01
Suez (1)	*Dinocardumvanhyningi*	4.17	86.31
Suez (2)	*Brachidontes* sp.	1.15	83.78
Ras Gharib (1)	*Nassariusclathratus*	7.06	77.02
Ras Gharib (2)	*Patella testudinaria*	19.72	71.89
NIOF (Hurghada) (1)	*Lepidochitoncinereus*	6.54	74.23
NIOF (Hurghada) (2)	*Neritawaigiensis*	4.28	65.74
Safaga (1)	*Lepidochitoncinereus*	6.63	69.97
Safaga (2)	*Morulasquamosa*	9.34	72.64
Quseir	*Neritapeloronta*	2.89	73.69
Marsa Alam	*Lepidochitoncinereus*	6.54	70.8
Shalateen Rahaba	*Neritaundata*	3.77	63.58

Table 2 PAH concentration (ppb) in IAEA – 406 reference material.

PAHs	Recommended	Found	Recover %
Naphthalene	24.00	22.92	95.50
Acenaphthylene	8.00	7.75	96.87
Acenaphthene	1100.00	1088.25	98.93
Phenanthrene	22.00	21.46	97.55
Anthracene	19.00	18.53	97.47
Fluoranthene	4.90	4.69	95.71
Pyrene	4.50	4.33	96.22
Benzo(a)anthracene	0.81	0.78	96.30
Chrysene	2.30	2.22	96.52
Benzo(b)fluoranthene	2.30	2.19	95.22
Benzo(k)fluoranthene	2.80	2.71	96.79
Benzo(a)pyrene	2.90	2.83	97.59
Beno(ghi)perylene	0.78	0.75	96.15

showed in Fig. 2. *n*-Alkanes (C_8–C_{40}) were found to be in the range of 71.0–701.1 ng/g with a mean value of 242.2 ± 192.1 ng/g dry wt. These results were higher than those obtained by our previous study (El Nemr et al., 2004) in which the total *n*-alkane concentration in the bivalve tissues from the Red Sea varies in the range of 8–425 ng/g dry wt. These values were lower than those reported for the Arabian Gulf and the Gulf of Oman, which ranged from 810–5300, 1200, 1600–2100 and 1600–6300 ng/g dry wt. (Tolosa et al., 2005).

The shellfish collected from the location of Marsa Alam were found to be the most polluted (701.1 ng/g dry wt.), while those collected from the location of Shalateen Rahaba were the least polluted (71.0 ng/g dry wt.). The variation in *n*-alkanes contents may be due to the anthropogenic sources (shipping activities, industrial discharges and sewage) and the inputs from natural sources (microbial activity, submerged or floating macrophytes and emergent terrestrial plants, Oyo-Ita et al., 2010).

Aquatic algae (both micro- and macro-algae) and photosynthetic bacteria are dominated by the C_{15}, C_{17}, and C_{19}, whereas, the vascular plants dominated by C_{27}, C_{29}, and C_{31} *n*-alkanes. The *n*-alkanes abundance in them reflects the sources of organic matter (Choudhary et al., 2010).

Table 3 shows the total *n*-alkanes (C_8–C_{40}) concentration and the diagnostic criteria that is useful for the origins identification of the *n*-alkanes. The long-chain *n*-alkanes (LHC, $>C_{23}$) was found to contain higher concentrations than the short-chain *n*-alkanes (SHC, $<C_{23}$). As for the distribution patterns, they showed large contributions from even (C_{26}, C_{28}, C_{30}) and odd carbons (C_{27}, C_{29}, C_{31}) (Fig. 3). For LHC *n*-alkanes, the C_{27} and C_{29} are diagnostic of waxes from trees and shrubs while the *n*-C_{31} is diagnostic of grass waxes (Jeng, 2007). The ratios of LHC/SHC showed values ranging from 0.62 to 6.35 (Table 3). The ratios obtained for Safaga (1) and (2) were at high values (6.33–6.35) and were dominated by higher plant and/or macrophyte waxes, whereas samples from Quseir, Shalateen Rahaba, Ras Suder and Suez (A) showed low values (0.62–1.88) and were dominanted by phytoplankton-derived organic matter (Commendatore et al., 2012). Samples from the rest of the stations reported intermediate values, suggesting a mixture of both input sources with no particular dominant trend (Oyo-Ita et al., 2010; El Nemr et al., 2013). The anthropogenic source may be petroleum and/or from recycled organic matter washed by rains or from effluents of treatment plants. The biogenic sources may be algae, plankton, marine animals, bacteria or terrestrial vascular plants (Commendatore et al., 2012).

A number of indices were calculated to identify the hydrocarbon sources found in the shellfish samples collected from the 13 different locations, and they were:

- Carbon preference index (CPI) representing the predominance of odd over even *n*-alkanes (Allan and Douglas, 1977):

$$\mathrm{CPI} = \frac{\sum (C_{23} - C_{31})_{\mathrm{odd}} + \sum (C_{25} - C_{33})_{\mathrm{odd}}}{2\sum (C_{24} - C_{32})_{\mathrm{even}}}$$

- Terrigenous aquatic ratio (TAR) quantifying the in situ algal vs. terrestrial organic matter (Bourbonniere and Meyers, 1996):

$$\mathrm{TAR} = \frac{C_{27} + C_{29} + C_{31}}{C_{15} + C_{17} + C_{19}}$$

- A proxy ratio (P_{aq}) quantifying the different plant types (e.g. submerged vs. emergent plant types) (Ficken et al., 2000):

$$P_{\mathrm{aq}} = \frac{C_{23} + C_{25}}{C_{23} + C_{25} + C_{29} + C_{31}}$$

- The natural *n*-alkanes ratio (NAR) roughly estimates the proportions of natural and petroleum *n*-alkanes (Mille et al., 2007).

$$\mathrm{NAR} = \frac{\sum n\text{-alkanes}(C_{19-32}) - 2\sum \text{even of } n\text{-alkanes}(C_{20-32})}{\sum n\text{-alkanes}(C_{19-32})}$$

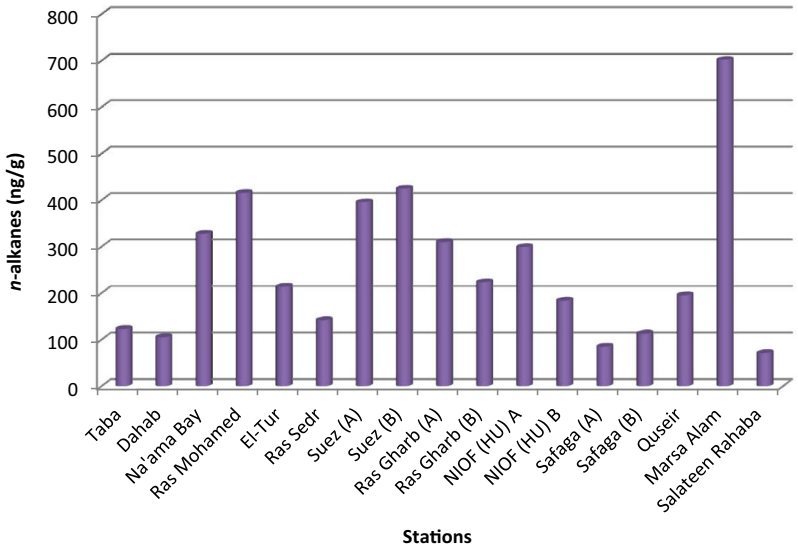

Figure 2 Distribution of *n*-alkanes in the collected shellfish samples from the studied locations.

Table 3 Concentration of *n*-alkanes (ng/g dry wt.) and calculated distribution indices in shellfish samples collected from the Gulf of Suez, Gulf of Aqaba and The Red Sea Proper coasts.

Station	$\sum C_8$–C_{40}	LHC/SHC	CPI	*n*-Alkane/C_{16}	TAR	ACL	P_{aq}	NAR
Taba	122.8	2.53	0.83	1642.2	4.36	28.78	0.04	−1.93
Dahab	105.3	2.47	2.68	231.2	3.66	27.62	0.15	−1.59
Na'ama Bay	327.2	1.50	1.52	696.1	9.15	30.35	0.06	−1.73
Ras Mohamed	415.2	2.17	1.44	708.1	11.78	30.10	0.06	−1.8
El-Tur	213.6	3.16	1.01	5225.4	2.83	27.65	0.26	−1.83
Ras Suder	141.6	1.58	6.24	1030.1	10.7	26.99	0.78	−1.59
Suez (1)	395.3	1.88	0.14	1336.0	5.29	26.93	1.00	−1.76
Suez (2)	424.3	3.43	0.15	1484.3	2.78	28.21	0.12	−1.76
Ras Gharb (1)	309.6	2.01	1.04	99.3	1.98	29.93	0.26	−1.78
Ras Gharb (2)	223.4	2.73	1.12	913.5	4.32	30.15	0.25	−1.8
NIOF (HU) 1	298.8	2.81	0.71	3670.9	2.59	29.72	0.08	−1.9
NIOF (HU) 2	183.5	3.25	0.68	0.0	2.08	27.86	0.13	−1.87
Safaga (1)	84.7	6.33	0.70	722.6	3.29	27.92	0.16	−1.71
Safaga (2)	112.8	6.35	1.45	621.6	3.43	28.52	0.14	−1.74
Quseir	195.2	0.62	0.67	2455.4	5.26	27.53	0.15	−1.82
Marsa Alam	701.1	2.09	1.03	766.5	12.28	29.89	0.13	−1.75
Salateen Rahaba	71.0	1.38	1.08	710.3	5.51	29.25	0.12	−1.76
Mean	254.4	2.74	1.35	1312.6	5.44	28.66	0.24	−1.77
SD	164.0	1.59	1.43	1349.8	3.53	1.22	0.26	0.09

LHC/SHC ratio: $\Sigma > C_{23}/\Sigma < C_{23}$.
CPI: carbon preference index, TAR: terrigenous/aquatic ratio, ACL: average carbon length, NAR: natural *n*-alkane ratio.

Carbon preference index (CPI)

Hydrocarbons in coastal marine environments are generally dominated by inputs from terrigenous sources. For example, the *n*-alkane of long-chain (C_{25}–C_{35}) distribution exhibited high odd-to-even predominance, which differentiated between alkanes from vascular land plants from the alkanes belonging to bacteria and petroleum. The carbon preference index (CPI) is the common parameter obtained from this predominance; it is an indication of the source of *n*-alkane. *n*-Alkanes from land plant originating material showed a predominance of odd-numbered carbon chains with CPI∼ 5–10 (Commendatore et al., 2012; Kanzari et al., 2014). This study highlights that in the location of Ras Suder the CPI value was 6.24, whereas petrogenic inputs had a CPI approximately <1.0 (Pendoley, 1992) as in most studied locations. The values of CPI close to one are due to more input of recycled organic matter and/or marine microorganisms (Kennicutt et al., 1987). The CPI is also used to indicate the presence of straight-chain geolipids in organic geochemistry (Meyers and Ishiwatari, 1995).

Average chain length (ACL)

The average chain length (ACL) is another method applied to study the source of *n*-alkanes in environment based on the concentration of the odd-carbon-numbers of the *n*-alkanes of

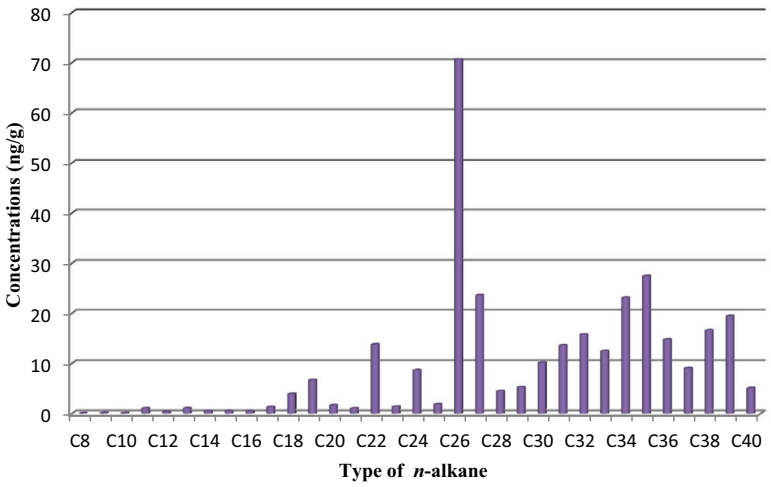

Figure 3 Variation of types of the *n*-alkane concentration in the collected shellfish samples from the studied locations.

higher plant (Poynter and Eglinton, 1990). The vegetation type is the main influence on the length of the chain that belongs to the terrigenous leaf lipids. Lipids in leaf are derived from plants in forests may on average have shorter chain lengths than lipids in leaf from grasslands (Cranwell, 1973). In the warmer climates, plants produce a longer-chain of *n*-alkanes (Jeng, 2006). The ACL is very useful in the identification of the environmental changes of a particulate ecosystem. Little environmental changes occurring in a system are characterized by a constant value of ACL (Sakari et al., 2008). In the present study, it was noticed that there are no considerable changes in the values of ACL between the studied locations, which may indicate that no environmental changes took place in the ecosystem (Table 3).

Both CPI and ACL are obtained using the *n*-alkanes data derived from higher plants, therefore, CPI and ACL are expected to correlate (Jeng, 2006). In the present study, the correlation between the CPI and ACL values of the shellfish samples show that there is no correlation between CPI and ACL ($r = 0.059$); which may be attributed to the fact that both CPI and ACL were not from the same source of higher plants. It was also noted that when two (or more) *n*-alkanes that are characterized by different values of ACL or CPI, their ratio values usually varies nonlinearly and disproportionately (Jeng, 2006).

Terrigenous/aquatic ratio (TAR)

A predominance of odd numbered (C_{27}, C_{29}, and C_{31}) *n*-alkanes is a characteristic of the debris of higher plants from terrestrial (Rieley et al., 1991), while the predominance of odd numbered (C_{15}, C_{17}, and C_{19}) *n*-alkanes indicates aquatic sources (Jaffé et al., 2001). The TAR, which is the ratio between the concentrations of short-chain to long-chain *n*-alkanes, can be used to evaluate the importance of terrigenous inputs in comparison to aquatic ones. This study showed TAR ratio >1 for all studied locations, which assured that the source of the *n*-alkanes is from debris of higher plant from terrestrial (Bourbonniere and Meyers, 1996).

Natural n-alkane ratio (NAR)

In petroleum hydrocarbons and crude oils, the NAR ratio is close to zero while in marine or higher terrestrial plants NAR ratio is close to 1. In the present study, the NAR ratio was close to 1, hence indicating that the hydrocarbons were from higher terrestrial plants or marine plant sources for most of the studied locations, results were given in Terrigenous/Aquatic Ratio (TAR). To study the long-chain *n*-alkanes origin in the shellfish (i.e., the long-chain *n*-alkanes derived from either macrophytes or higher plant wax), the P_{aq} was calculated and found to range from 0.04 to 1.0 (Table 3). Ficken et al. (2000) reported that the P_{aq} values are ranging from 0.01 to 0.23 in terrestrial plant waxes, whereas the values of P_{aq} in the range from 0.48 to 0.94 are belonging to submerged/floating macrophytes. Generally, our results showed the contribution of both the higher plant/macrophyte waxes derived, and the phytoplankton-derived organic carbon.

From all the studied ratios (CPI, ACL, TAR, Paq, and NAR), it can be concluded that the *n*-alkanes found in collected shellfish from the Gulf of Suez, Gulf of Aqaba and the Red Sea are mainly from recycled organic matter and/or marine microorganisms.

Distribution and sources of polycyclic aromatic hydrocarbons (PAHs)

Table 4 shows the names and some features of the detected PAHs in this study. Total PAH (ΣPAHs) concentrations in shellfish that were collected from the studied locations, varied significantly. The values ranged from 1.25 to 160.9 ng/g dry wt. with an average of 47.9 ± 45.5 ng/g dry wt. (Table 5). The highest concentrations of ΣPAHs were recorded in the shellfish collected from Ras Suder (160.9 ng/g dry wt.), followed by those from Suez 1 (105.96 ng/g dry wt.), Safaga 2 (95.52 ng/g dry wt.) and Suez 2 (64.04 ng/g dry wt.). This indicated a wide range of PAHs from different sources such as municipal, agriculture and industrial effluent as well as oil spills at these locations (Table 6). Lower concentrations of

Table 4 The abbreviation, source molecular formula, molecular weight (MW) and carcinogenicity index of PAHs.

Compound name (IUPAC)	No. of rings	Source	Abbreviation	Molecular formula	Molecular weight	Carcinogenicity (USEPA, 2011)
Naphthalene	2	Petro	Naph	$C_{10}H_8$	128.2	0
Acenaphthylene	3	Petro	Acey	$C_{12}H_8$	152.2	0
Acenaphthene	3	Petro	Ace	$C_{12}H_8$	152.2	0
Fluorene	3	Petro	Fl	$C_{13}H_{10}$	166.2	0
Phenanthrene	3	Petro	Phe	$C_{14}H_{10}$	178.2	0
Anthracene	3	Petro	Ant	$C_{14}H_{10}$	178.2	0
Fluoranthene	4	Petro	Flu	$C_{16}H_{10}$	202.2	0
Pyrene	4	Petro	Pyr	$C_{16}H_{10}$	202.2	0
Benzo[a]anthracene	4	Petro	BaA	$C_{18}H_{12}$	228.3	+ +
Chrysene	4	Petro	Chry	$C_{18}H_{12}$	228.3	+ +
Benzo[b]Fluoranthene	5	Pyro	BbF	$C_{20}H_{12}$	252.3	+ +
Benzo[k] Fluoranthene	5	Pyro	BkF	$C_{20}H_{12}$	252.3	+ +
Benzo[a]Pyrene	5	Pyro	BaP	$C_{20}H_{12}$	252.3	+ + +
Dibenzo[ah]anthracene	5	Pyro	DahA	$C_{22}H_{14}$	278.3	+ + +
Benzo(ghi)perylene	6	Pyro	BghiP	$C_{22}H_{12}$	276.3	0
Indeno(1,2,3-c,d)pyrene	6	Pyro	InP	$C_{22}H_{12}$	276.3	+ + +

USEPA: United States Environmental Protection Agency; 0 = not carcinogenic, + +, + + + = strongly carcinogenic, petro (petrogenic); Pyro (pyrolytic).

Table 5 Concentrations of different PAHs (ng/g dry wt.) in shellfish samples collected from the Gulf of Suez, Gulf of Aqaba and The Red Sea Proper coasts.

Stations	D	NB	RM	ET	RS	S1	S2	RG1	RG2	N1	N2	SF1	SF2	ShR
Naph	ND	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.22	ND	ND
Acey	0.11	0.03	0.10	0.11	0.23	ND	ND	ND	ND	ND	ND	0.14	ND	ND
Ace	1.42	0.62	0.18	0.10	2.02	1.12	1.51	0.99	ND	24.74	2.63	0.40	0.48	0.09
Fl	0.63	0.51	0.23	0.14	0.67	1.59	1.68	0.30	0.27	1.03	0.71	0.23	1.47	ND
Phe	1.10	3.19	0.23	0.70	4.15	5.76	4.95	1.23	0.36	1.61	1.63	2.81	11.07	0.02
Ant	0.96	0.86	3.64	0.86	2.74	2.96	3.59	2.57	0.50	0.99	0.77	17.51	51.59	ND
Flu	0.76	0.69	2.45	5.72	2.07	10.70	8.55	1.98	0.87	15.58	11.70	5.29	6.76	0.06
Pyr	0.77	0.51	5.31	1.16	1.75	4.60	8.15	4.55	1.72	1.50	3.62	6.31	15.36	0.02
BaA	0.27	0.21	0.41	0.41	0.52	2.38	0.83	0.53	1.43	1.06	18.23	1.31	2.00	0.88
Chry	34.76	3.36	0.68	0.19	144.75	74.74	32.85	0.94	0.36	0.13	0.18	0.57	1.04	0.02
BbF	0.15	0.23	0.09	0.56	0.16	0.54	0.27	0.56	2.91	4.41	2.03	0.02	0.04	0.11
BkF	0.44	1.10	0.42	0.29	0.27	0.89	1.06	0.62	0.79	0.58	0.36	0.15	0.55	0.02
BaP	0.48	1.52	2.30	1.25	1.02	0.11	0.15	0.34	0.31	0.20	0.04	1.18	4.25	0.02
DahA	0.16	0.16	0.06	0.24	0.29	0.03	0.04	0.09	0.16	0.05	0.02	0.24	0.09	ND
BghiP	0.27	0.76	0.20	0.03	0.13	0.26	0.24	0.10	1.67	0.35	0.10	0.60	0.67	0.01
InP	0.19	0.29	0.24	0.01	0.16	0.28	0.18	0.07	0.25	0.56	0.16	0.29	0.15	0.02
Total PAHs	42.47	14.04	16.53	11.76	160.92	105.96	64.04	14.88	11.61	52.79	42.16	37.06	95.52	1.27
BaA/Chry	0.01	0.06	0.60	2.21	0.00	0.03	0.03	0.56	3.97	7.92	100.54	2.29	1.93	42.72
InP/BghiP	0.71	0.39	1.24	0.39	1.25	1.07	0.76	0.70	0.15	1.60	1.63	0.47	0.22	2.00
Fl/(Fl + Pyr)	0.45	0.50	0.04	0.11	0.28	0.26	0.17	0.06	0.14	0.41	0.16	0.04	0.09	0.04
Ant/(Ant + Phe)	0.47	0.21	0.94	0.55	0.40	0.34	0.42	0.68	0.58	0.38	0.32	0.86	0.82	0.05
BaA/(BaA + Chry)	0.01	0.06	0.37	0.69	0.00	0.03	0.02	0.36	0.80	0.89	0.99	0.70	0.66	0.98
InP/(IP + BghiP)	0.42	0.28	0.55	0.28	0.56	0.52	0.43	0.41	0.13	0.62	0.62	0.32	0.18	0.67

D = Dahab; NB = Na'ama Bay; RM = Ras Mohammed; ET = El Tour; RS = Ras Suder; S1 = Suez (1); S2 = Suez (2); RG 1 = Ras Gharib (1); RS 2 = Ras Gharib (2); N1 = NIOF (Hurghada-1); N2 = NIOF (Hurghada-2); SF 1 = Safaga (1); SF 2 = Safaga (2); ShR = Shalateen Rahaba.

ΣPAHs were detected in Ras Ghareb 2, El Tour, Na'ama Bay and Ras Ghareb 1 (11.61, 11.76, 14.04 ng/g dry wt., respectively). The variation in PAH content in the shellfish samples along the Red Sea coast may be related to variable sources of discharged waters, proximity to fuel combustion emissions and human activities. These results were lower than those obtained by a previous study of some selected locations of the Red Sea by El Nemr et al. (2004), in which the concentration of total PAHs in the mussel tissues from the Red Sea varied in the range of 676–4666 ng/g dry wt. The PAHs values of the present study are lower than those recorded in the study done in the Arabian Gulf and Gulf of Oman to determine the concentrations of PAHs in bivalves collected from different sites in different countries (United Arab Emiraes, Qatar, Bahrain and Oman), which are known by their oil pollution. It was found that their concentrations of PAHs ranged from

Table 6 Sources of pollution and other impacts and the main sites of pollution in the Gulf of Suez, Gulf of Aqaba and the Red Sea proper.

Sources of Pollution and others impacts	Main sites of pollution
Taba	Sewage and tourist resorts
Dahab	Sewage and tourist resorts
Na'ama Bay	Sport activities (boat grounding snorkeling or SCUBA-diving tourists)
Ras Mohamed	Nature reserve (protected area)
El Tour	Oil pollution from shipping
Ras Suder	Sewage and tourist resorts
Suez	Sewage, agricultural and garbage wastes, effluents oil refineries (SUMED oil pipeline), fertilizer plants wastes and tourist resorts
Ras Gharb	Oil pollution from shipping, sewage and agricultural wastes and tourist resorts
NIOF (Hurgada)	Oil pollution from fish processing activities and tourist centers
Safaga	Shipment of mineral products from phosphate and aluminum mines in the Eastern Desert
Marsa Alam	Sewage and fish processing activities
Shalateen Rahaba	Sewage and fish processing activities

$(36.6–846) \times 10^3$, 105×10^3, $(58.3–105) \times 10^3$ and $(17–173) \times 10^3$ ng/g dry wt. (Tolosa et al., 2005).

There was an insignificant correlation ($r = 0.002$) observed between ΣPAHs and *n*-alkane, which may reflect the effects of the direct inputs of different locations on the distribution and concentrations of PAHs. It was documented that the petroleum hydrocarbon concentrations were due to the influence of the local inputs and the localities influenced by human activities (Bixiong et al., 2007). This conclusion can be observed in Table 6 that summarizes the different sources of pollutions along the Red Sea coast. Fig. 4 shows that Chrysene is the most abundant PAH in the shellfish collected from the Red Sea coast (294.6 ng/g dry wt.), followed by Anthracene (89.5 ng/g dry wt.), Fluoranthene (73.2 ng/g dry wt.) and Pyrene (55.3 ng/g dry wt.). Chrysene concentration is elevated at Dahab (34.76 ng/g dry wt.), Ras Suder (144.75 ng/g dry wt.), Suez 1 (74.74 ng/g dry wt.) and Suez 2 (32.85 ng/g dry wt.) which may be attributed to small past oil spill near these locations (Stogiannidis and Laane, 2015). As reported further degradation of oil spill leads to the enhancement of the chrysene concentration relative to other PAH series, and to a significant decrease in the relative ratios of the sum of naphthalenes, phenanthrenes, dibenzothiophenes, and fluorenes, to chrysenes (Stogiannidis and Laane, 2015).

Car-PAHs [benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene] are eight PAHs typically considered as possible carcinogens (IARC, 1983). Benzo(a)pyrene is the highly carcinogenic PAH (Wang et al., 2002). The highest concentration value of the ΣPAH_{CARC} was the value recorded at Ras Suder with a concentration of 147.2 ng/g dry wt., which also recorded the highest carcinogenic PAH percentage (% CARC = 91.5%). This indicates the adverse effect of these shellfish on human health (Table 7).

The ratio of the sum belonging to the major combustion specific compounds (ΣCOMB = Pyr, Flu, BbF, BaA, Chry, BaP, InP, BghiP, and BkF) to the sum of 16 EPA-PAHs (% ΣCOMB/ΣPAHs) ranged from 32.4% to 93.9% and the ΣCOMB concentrations displayed values from 1.1 to 149.4 ng/g dry wt. (Table 7); The high ratio values of ΣCOMB/ΣPAHs further indicated an extensive combustion activities affected the PAH concentration in the shellfish samples collected from the Egyptian coast of the Red Sea.

In order to characterize the PAHs in respect to their sources, some diagnostic ratios were considered (El Nemr, 2008; El Nemr et al., 2007, 2012). To assess the combustion (pyrogenic) and petroleum inputs, the ratios of some PAHs such as Phen/Ant, Flu/Py, Flu/(Flu + Py), and Flu/(Flu + Phe) were also calculated (Shi et al., 2007). Petroleum often contains more thermodynamically stable PAHs (e.g., Phe) than the less stable PAHs (e.g., Ant). Therefore, PAHs from petroleum usually have high Phen/Ant ratios. Bivalves with Phen/Ant > 10 are mainly contaminated by petroleum hydrocarbons, and bivalves with Phen/Ant < 10 are typical

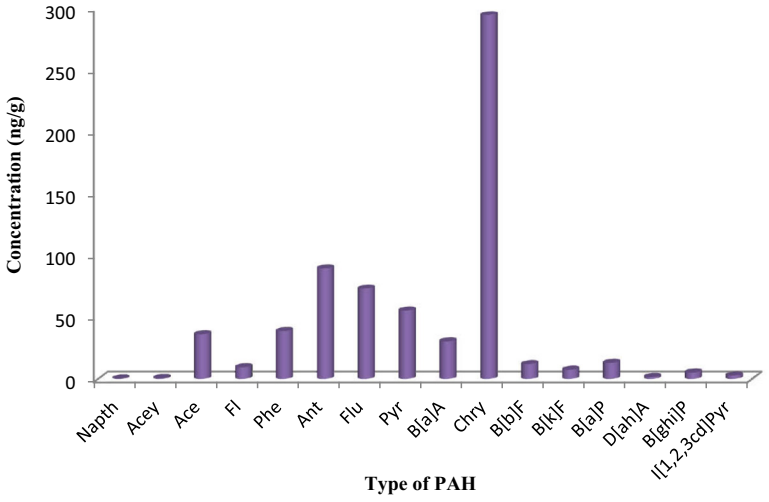

Figure 4 Variation of types of PAH concentrations in the collected shellfish samples from the studied locations.

Table 7 Total Polycyclic aromatic hydrocarbons (∑PAHs), pyrolytic (ΣCOMB), %∑COMB/∑PAHs, carcinogenic PAHs, % CARC, fossil (ΣPAH), %∑FPAH/∑PAH, Flu/Pyr, phen/Ant, BaA/Chr and ∑F-PAH/∑COMB in shellfish samples collected from the Gulf of Suez, Gulf of Aqaba and The Red Sea Proper coasts.

Location	∑PAHs	∑COMB	%∑COMB/∑PAHs	PAHCARC	% CARC	∑F-PAH	%∑FPAH/∑PAH	Flu/Pyr	Phe/Ant	BaA/Chr	∑F-PAH/∑COMB
Dahab	42.5	38.1	90.1	36.7	86.5	4.2	9.9	0.99	1.14	0.01	0.11
Na'ama Bay	14.0	8.5	62.3	7.6	54.4	5.3	37.8	1.37	3.69	0.06	0.60
Ras Mohamed	16.5	9.9	73.5	4.4	26.6	4.4	26.5	0.46	0.06	0.59	0.36
El Tour	11.8	4.0	83.7	3.0	25.3	1.9	16.2	4.91	0.81	2.20	0.19
Ras Suder	160.9	149.4	93.9	147.2	91.5	9.8	6.1	1.18	1.51	0.01	0.06
Suez 1	106.0	85.4	89.2	79.2	74.8	11.4	10.7	2.32	1.94	0.03	0.12
Suez 2	64.0	45.4	81.6	35.6	55.6	11.7	18.3	1.05	1.38	0.03	0.22
Ras Ghareb 1	14.9	8	65.7	3.3	21.9	5.1	34.2	0.44	0.48	0.56	0.52
Ras Ghareb 2	11.6	9.7	90.3	7.9	67.9	1.1	9.7	0.51	0.73	3.97	0.10
NIOF (Hu) 1	52.8	9.8	46.3	7.4	13.9	28.4	53.7	10.4	1.61	7.90	1.16
NIOF (Hu) 2	42.2	25.4	86.4	21.1	50.1	5.7	13.5	3.24	2.12	100.00	0.15
Safaga 1	37.1	10.6	43.1	4.4	11.8	21.3	57.5	0.84	0.16	2.29	1.33
Safaga 2	95.5	25.5	32.4	8.8	9.2	64.6	67.6	0.44	0.21	1.92	2.09
Shalateen Rahaba	1.3	1.1	91.5	1.1	84.8	0.1	8.4	2.38	0.00	42.70	0.09

impacted by combustion residues (Unlü and Alpar, 2006). In the present study, the ratio of individual PAH compounds was almost stable in all locations indicating that the sources of PAH contamination might be the same. The Phe/Ant ratio (< 10) is recorded in all stations (Table 7) indicating pyrolytic source (Tsapakis et al., 2003). Certain PAH components ratios of the same molecular weight are well established as an index to study PAH composition and deduce their possible sources (Yunker et al., 1996). Each source of PAHs may provide a signature or an individual profile, which can be used in the source identification of the PAHs (Kannan et al., 2005). PAH concentration ratios of the same molecular weight such as Flur/(Flur + Pyr) and Ant/(Ant + Phe) were used to study the possible sources of PAHs. Fig. 5 shows the PAHs molecular ratios in bivalves at different sampling sites in this study. Ant/(Ant + Phe) ratios in all of the studied location were mostly higher than 0.1 with an average of 0.49, except in Shalateen Rahaba in which the value is 0. The ratio's data showed that the PAHs might be derived from combustion sources. The Flur/(Flur + Pyr) ratios were mostly higher than 0.5 with an average of 0.55, showing that the wood, grass and coal combustion could be the possible sources of PAHs. The combustion of crop residues might be the possible source of PAHs in seawater and consequently in the bivalves. However, Flur/(Flur + Pyr) ratios in biota from Ras Mohamed, Ras Ghareb 1, Ras Ghareb 2, Safaga 1, NIOF (Hu) 2 were below 0.5 showing some petrogenic input of PAHs. Fig. 6 shows evidence of more contributions from petroleum combustion of PAHs for all stations. Shellfish samples contaminated with PAHs, that present Ant/(Ant + Phe) ratio > 0.10 and Fl/(Fl + Pyr) ratio > 0.50, show that combustion products are predominant. It was the same case for BaA/(BaA + Chry) ratio > 0.35 that is together associated with Fl/(Fl + Pyr) ratio > 0.40. Thus, the PAH isomer ratios showed that the PAHs in shellfish samples of the studied locations were mainly derived from combustion sources (Kanzari et al., 2014).

The distribution of different PAHs rings also indicates different sources of the PAHs from petrogenic and pyrogenic origins. This is because PAHs from a petrogenic origin predominantly consist of lower molecular weights (two and three

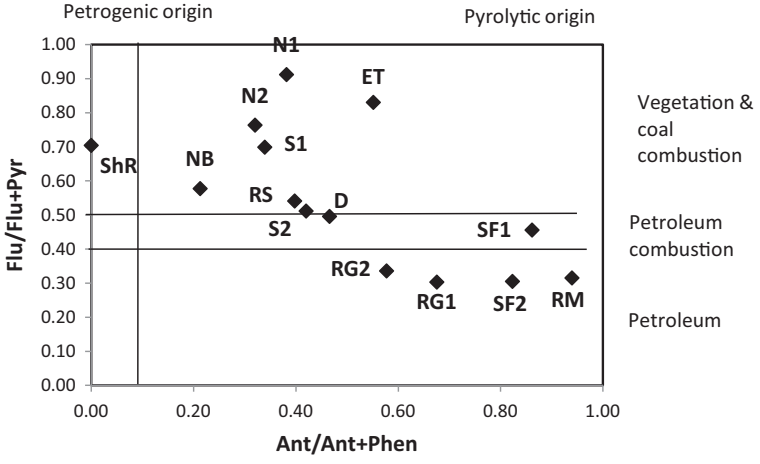

Figure 5 PAH cross plots for the isomer ratios of Ant/(Ant + Phe) vs. Flur/(Flur + Pyr) (Average represents the ratio of average concentration of sampling stations).

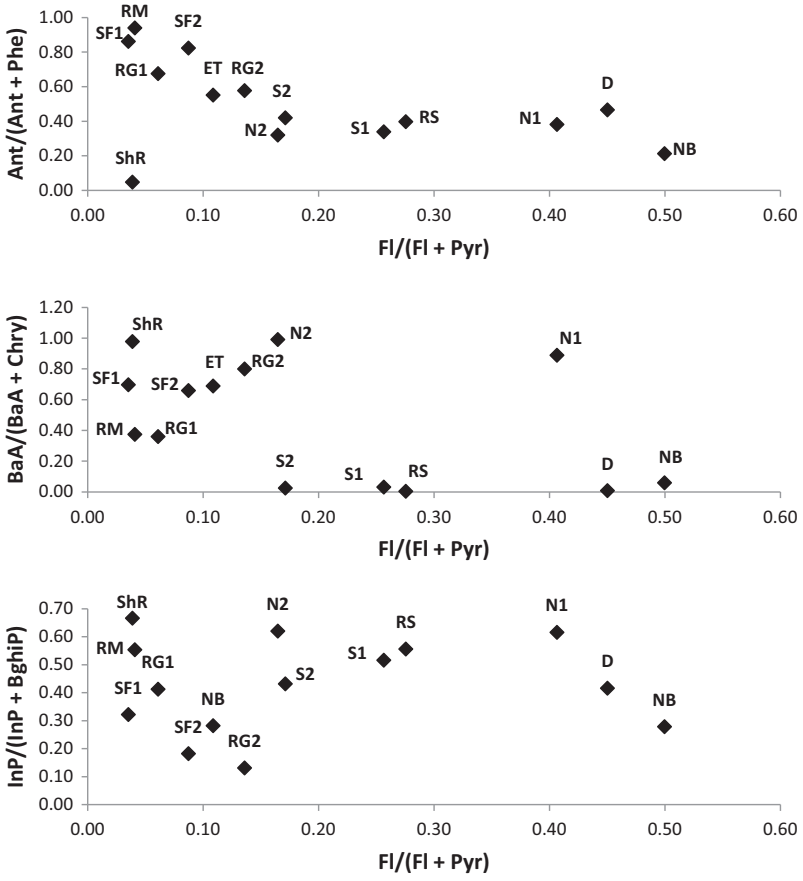

Figure 6 Plot of Ant/(Ant + Phe) (a), BaA/(BaA + Chry) (b) and IP/(IP + BghiP) (c) against Fl/(Fl + Pyr).

rings), whereas the pyrogenic origin PAHs generally have higher molecular weights, such as four- and five-ring PAH species (Kannan et al., 2005). PAH carcinogenic potency was divided into three groups of (2 + 3)-, 4-, (5 + 6)-ring. Fig. 7 shows the triangular diagram of percentage average concentrations of different ring number PAHs in different sampling location (Wang et al., 2011; Shao et al., 2014). Fig. 7 shows

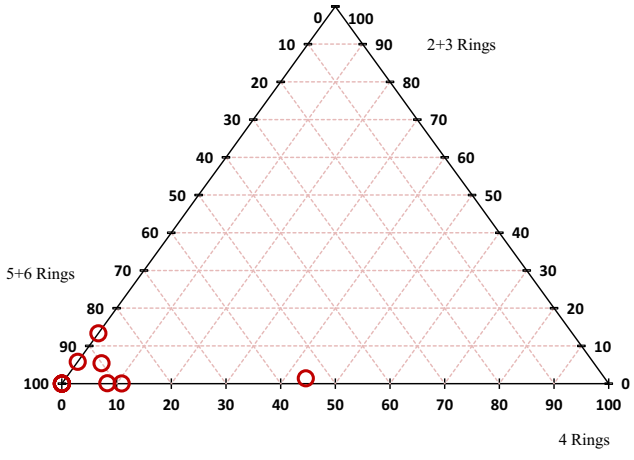

Figure 7 Triangular diagram of percentage average concentrations for the 16 PAHs in the collected shellfish samples from the studied locations.

that the PAHs of 4, 5 or 6 rings are the abundant PAHs in the shellfish collected along the Red Sea coast (73.94%), while those of 2 and 3 rings represent 26.17% of total PAHs. These results indicated that the source of PAHs in most studied locations mainly came from pyrolytic origin. The results reveal how pyrolytic sources were the main contributors in the shellfish along the Red Sea coast while few petrogenic inputs of PAHs also existed.

Cancer risk assessment

The BaP-equivalent (BaPE) is used as a safer way to assess the carcinogenic risk due to the contamination by PAHs. The BaPE not only included the risk due to BaP, but it also calculated all of the carcinogenic PAHs, where each of PAH weighed according to its carcinogenicity in relation to the carcinogenicity of BaP, which is measured by 1. This index can be calculated by the next equation (Liu et al., 2009).

$$\mathrm{BaPE} = \mathrm{BaP} + (\mathrm{BaA} \times 0.06) + (\mathrm{BkF} \times 0.07) + (\mathrm{BbF} \times 0.07) + (\mathrm{DBA} \times 0.60) + (\mathrm{InP} \times 0.08)$$

BaPE ranges from 0.079 to 4.47 with an average of 1.25 ng/g. Fig. 8 indicates that the higher values of BaPE were in Safaga 2, followed by Ras Mohamed and Na'ama Bay hence indicating that PAHs in these sites have high carcinogenic effects.

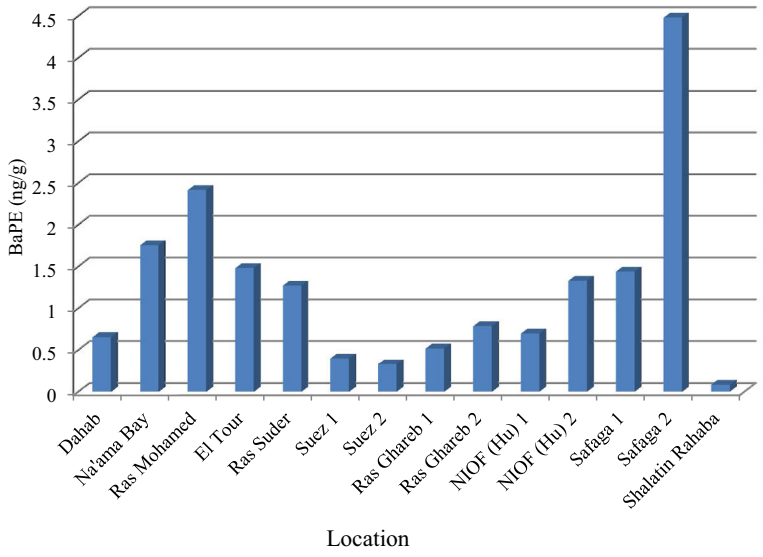

Figure 8 BaPE values in the collected shellfish samples from the studied locations.

Conclusion

This study provides valuable information about the distribution, transport and sources of *n*-alkanes and PAHs in the shellfish samples obtained from the Suez Gulf, Aqaba Gulf and the Red Sea proper. The *n*-alkanes found in collected shellfish from the Gulf of Suez, Gulf of Aqaba and the Red Sea proper were mainly from recycled organic matter and/or marine microorganisms. A total concentration of 16 PAHs ranged from 1.25 to 160.9 ng/g dry wt. in the shellfish of the Red Sea coast. The PAH concentration in the shellfish samples can be classified as low concentration levels. Therefore, now, the adverse effects and toxicity of PAHs on the exposed bio-organisms in the studied area are of low concern. This study show that the sources of PAHs obtained through the use of diagnostic ratios are from both pyrogenic and petrogenic sources derived from combustion (through atmospheric input) and also from fresh petrogenic inputs with a dominance of pyrogenic PAHs. The BaP-equivalent (BaPE) was high at Safaga, Ras Mohamed and Na'ama Bay.

Conflicts of interest

The authors declare that there are no conflicts of interest.

References

Allan, J., Douglas, A.G., 1977. Variations in the content and distribution of *n*-alkanes in a series of Carboniferous vitrinites and sporinites of bituminous rank. Geochim. Cosmochim. Acta 41, 1223–1230.

Bixiong, Y., Zhihuan, Z., Ting, M., 2007. Petroleum hydrocarbon in surficial sediment from rivers and canals in Tianjin, China. Chemosphere 68, 140–149.

Bourbonniere, R.A., Meyers, P.A., 1996. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. Limnol. Oceanogr. 41, 352–359.

Choudhary, P., Routh, J., Chakrapani, G.J., 2010. Organic geochemical record of increased productivity in Lake Naukuchiyatal, Kumaun Himalayas, India. Environ. Earth Sci. 60, 837–843.

Commendatore, M.G., Nievas, M.L., Amin, O., Esteves, J.L., 2012. Sources and distribution of aliphatic and polyaromatic hydrocarbons in coastal sediments from the Ushuaia Bay (Tierra del Fuego, Patagonia, Argentina). Mar. Environ. Res. 74, 20–31.

Cranwell, P.A., 1973. Chain-length distribution of *n*-alkanes from lake sediments in relation to post-glacial environmental change. Freshw. Biol. 3, 259–265.

El Nemr, A., 2005. Petroleum Contamination in Warm and Cold Marine Environment. Nova Science Publishers Inc, Hauppauge, New York, ISBN 1-59454-615-0, 150 pp.

El Nemr, A., 2008. Organic hydrocarbons in surface sediments of the Mediterranean coast of Egypt: distribution and sources. Egypt. J. Aquat. Res. 34 (3), 36–57.

El Nemr, A. (Ed.), 2011. Impact, Monitoring and Management of Environmental Pollution. Nova Science Publishers Inc, Hauppauge New York, ISBN-10: 1608764877, ISBN-13: 9781608764877, 638 pp.

El Nemr, A., El-Sikaily, A., Khaled, A., Said, T.O., Abd-Alla, A.M. A., 2004. Determination of hydrocarbons in mussels from the Egyptian Red Sea coast. Environ. Monit. Assess. 96, 251–261.

El Nemr, A., Said, T.O., Khaled, A., El-Sikaily, A., Abd-Allah, A.M. A., 2007. The distribution and sources of polycyclic aromatic hydrocarbons in surface sediments along the Egyptian Mediterranean coast. Environ. Monit. Assess. 124, 343–359.

El Nemr, A., El-Sikaily, A., Khaled, A., Ragab, S., 2012. Distribution patterns and risk assessment of hydrocarbons in bivalves from Egyptian Mediterranean coast. Blue Biotechnol. J. 1 (3), 457–472.

El Nemr, A., El-Sadaawy, M.M., Khaled, A., Draz, S.O., 2013. Aliphatic and polycyclic aromatic hydrocarbons in the surface sediments of the Mediterranean: assessment and source recognition of petroleum hydrocarbons. Environ. Monit. Assess. 185, 4571–4589.

El Nemr, A., El-Sadaawy, M.M., Khaled, A., El-Sikaily, A., 2014. Distribution patterns and risks posed of polycyclic aromatic hydrocarbons contaminated in surface sediment of the Red Sea coast (Egypt). Desalination Water Treat. 52, 7964–7982.

El Sikaily, A., Khaled, A., El Nemr, A., Said, T.O., Abd-Allah, A.M. A., 2003. Polycyclic aromatic hydrocarbons and aliphatic in the coral reef skeleton of the Egyptian Red Sea coast. Bull. Environ. Contam. Toxicol. 71 (6), 1252–1259.

Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. Org. Geochem. 31, 745–749.

IARC (International Agency for Research on Cancer), 1983. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Human, Polynuclear Aromatic Compounds, Part I, Chemical, Environmental, and Experimental Data. World Health Organization, Geneva.

Jaffé, R., Mead, R., Hernandez, M.E., Peralba, M.C., DiGuida, O.A., 2001. Origin and transport of sedimentary organic matter in two subtropical estuaries: a comparative, biomarker-based study. Org. Geochem. 32, 507–526.

Jeng, W.-L., 2006. Higher plant *n*-alkane average chain length as an indicator of petrogenic hydrocarbon contamination in marine sediments. Mar. Chem. 102, 242–251.

Jeng, W.L., 2007. Aliphatic hydrocarbon concentrations in short sediment cores from the southern Okinawa Trough: implications for lipid deposition in a complex environment. Cont. Shelf Res. 27, 2066–2078.

Kannan, K., Restrepo, B.J., Yohn, S.S., Gisey, J.P., Long, D.T., 2005. Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediments from Michigan inland lakes. Environ. Sci. Technol. 39, 4700–4707.

Kanzari, F., Syakti, A.D., Asia, L., Malleret, L., Piram, A., Mille, G., Doumenq, P., 2014. Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and pesticides) in surface sediments of an industrialized urban river (Huveaune), France. Sci. Total Environ. 478, 141–151.

Kelly, C.A., Law, R.J., Emerson, H.S., 2000. Methods for analysis for hydrocarbons and polycyclic aromatic Hydrocarbons (PAHs) in marine samples, <https://www.cefas.co.uk/publications/aquatic/aepam12.pdf>.

Kennicutt II, M.C., Barker, C., Brooks, J.M., DeFreitas, D.A., Zhu, G.H., 1987. Selected organic matter source indicators in the Orinoco, Nile and Changjiang deltas. Org. Geochem. 11, 41–51.

Liu, W.X., Dou, H., Wei, Z.C., Chang, B., Qiu, W.X., Liu, Y., Tao, S., 2009. Emission characteristics of polycyclic aromatic hydrocarbons from combustion of different residential coals in North China. Sci. Total Environ. 407, 1436–1446.

Meyers, P.A., Ishiwatari, R., 1995. Organic matter accumulation records in lake sediments. In: Lerman, A., Imboden, D.M., Gat, J. R. (Eds.), Physics and Chemistry of Lakes. Springer, Berlin, pp. 279–328.

Mille, G., Asia, L., Guiliano, M., Malleret, L., Doumenq, P., 2007. Hydrocarbons in coastal sediments from the Mediterranean sea (Gulf of Fos area, France). Mar. Pollut. Bull. 54, 566–575.

Neff, J.M., 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Source, Fates and Biological Effects. Applied Science publisher LTD, London.

Nudi, A.H., Wagener, A.L.R., Francioni, E., Sette, C.B., Sartori, A. V., Scofield, A.L., 2010. Biomarkers of PAHs exposure in crabs Ucidescordatus: laboratory assay and field study. Environ. Res. 110, 137–145.

Oyo-Ita, O.E., Ekpo, B.O., Orosa, D.R., 2010. Distributions and sources of aliphatic hydrocarbons and ketones in surface sediments from the Cross River estuary, S.E. Niger Delta, Nigeria. J. Appl. Sci. Environ. Sanit. 5 (1), 1–11.

Pendoley, K., 1992. Hydrocarbons in Rowley Shelf (Western Australia) oysters and sediments. Mar. Pollut. Bull. 24, 210–215.

Poynter, J.G., Eglinton, G., 1990. Molecular composition of three sediments from hole 717C: the Bengal Fan. In: Cochran, J.R., Stow, D.A.V., et al. (Eds.), . In: Proceedings of the Ocean Drilling Program Scientific Results, vol. 116, pp. 155–161.

Rieley, G., Collier, R.J., Jones, D.M., Eglinton, G., 1991. The biogeochemistry of Ellesmere Lake, UK I: source correlation of leaf wax inputs to the sedimentary record. Org. Geochem. 17, 901–912.

Saad, A.A., El Nemr, A., El-Sikaily, A.M., Mokhamer, E.-H., Khamis, M.A., 2015. Urinary metabolites and oxidative stress of polycyclic aromatic hydrocarbon as biomarker of exposure to environmental marine pollution. Int. J. Chem. Environ. Eng. 6 (2), 95–104.

Sakari, M., Zakaria, M.P., Junos, M.B.M., Annuar, N.A., Yun, H.Y., Heng, Y.S., Zainuddin, S.M.H.S., Chai, K.L., 2008. Spatial distribution of petroleum hydrocarbon in sediments of major rivers from east coast of peninsular Malaysia. Coast. Mar. Sci. 32 (1), 1–8.

Salem, D.M.S.A., Morsy, F.A.-E.M., El Nemr, A., El-Sikaily, A., Khaled, A., 2014. The monitoring and risk assessment of aliphatic and aromatic hydrocarbons (PAHs) in sediments of the Red Sea, Egypt. Egypt. J. Aquat. Res. 40, 333–348.

Shao, Y., Wang, Y., Xu, X., Wu, X., Jiang, Z., He, S., Qian, K., 2014. Occurrence and source apportionment of PAHs in highly vulnerable karst system. Sci. Total Environ. 490, 153–160.

Shi, Z., Tao, S., Pan, B., Liu, W.X., Shen, W.R., 2007. Partitioning and source diagnostics of polycyclic aromatic hydrocarbons in rivers in Tianjin, China. Environ. Pollut. 146, 492–500.

Stogiannidis, E., Laane, R., 2015. Source characterization of polycyclic aromatic hydrocarbons by using their molecular indices: an overview of possibilities. In: Whitacre, D.M. (Ed.), . In: Reviews of Environmental Contamination and Toxicology, vol. 234, pp. 49–133.

Tolosa, I., de Mora, S.J., Fowler, S.W., Villeneuve, J.-P., Bartocci, J., Cattini, C., 2005. Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from the Gulf and the Gulf of Oman. Mar. Pollut. Bull. 50, 1619–1633.

Tsapakis, M., Stephanou, E.G., Karakassis, I., 2003. Evaluation of atmospheric transport as a nonpoint source of polycyclic aromatic hydrocarbons in marine sediments of the Eastern Mediterranean. Mar. Chem. 80 (4), 283–298.

Unlü, S., Alpar, B., 2006. Distribution and sources of hydrocarbons in surface sediments of Gemlik Bay, Marmara Sea, Turkey. Chemosphere 64, 764–777.

USEPA, 2011. Evaluation of the Inhalation Carcinogenicity of Ethylene Oxide (Interagency Science Discussion Draft). U.S. Environmental Protection Agency, Washington, DC, EPA/600/P-03/007B.

Wang, X.L., Tao, S., Dawson, R.W., Xu, F.L., 2002. Characterizing and comparing risks of polycyclic aromatic hydrocarbons in a Tianjin wastewater-irrigated area. Environ. Res. 90, 201–206.

Wang, C., Sun, H., Chang, Y., Song, Z., Qin, X., 2011. PAHs distribution in sediments associated with gas hydrate and oil seepage from the Gulf of Mexico. Mar. Pollut. Bull. 62, 2714–2723.

Yunker, M.B., Snowdon, L.R., Macdonald, R.W., Smith, J.N., Fowler, M.G., Skibo, D.N., 1996. Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. Environ. Sci. Technol. 30 (4), 1310–1320.

Zemanek, M.G., Pollard, S.J.T., Kenefick, S.L., Hrudey, S.E., 1997. Multi-phaseportioning and co-solvent effects for polynuclear aromatic hydrocarbons (PAH) in authentic petroleum- and creosote-contaminated soils. Environ. Pollut. 98, 239–252.